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LIST OF TRANSLATED DOCUMENTS:

German Patent Application WO 2005/100459 A1, *Beschichtungsmaterial / Coating Material*

Signature: _____


Katja I. Suletzki, Latitude48 Translation

Date: _____

September 27, 2006

NOTARY STATEMENT

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) \$

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I, Ben Wisely, Notary Public in and for said County and State, do hereby certify that on this day, Katja I. Suletzki, personally known to me to be the same person and official who executed the above and foregoing statement appeared before me in person and acknowledged that she executed the above statement as her free and voluntary act.

Pursuant to authority conferred on me, I have signed and applied my seal on this day.



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Date: _____

September 27, 2006

COATING MATERIAL

The invention relates to a coating material comprising a binding agent and a filler containing particles having a size of less than 10 μm and/or a surface roughness of less than 10 μm or less [sic] as well as the use of such a coating material for the coating of facades and other parts of buildings.

Coating materials of the kind mentioned above are used for visual or construction physics-related reasons to coat facades and other construction surfaces. But the fact that the cleaning of the surfaces coated with such coating materials is often difficult and costly has turned out to be a problem. For this reason, efforts have been made for a long time to look for ways of creating self-cleaning designs of the surfaces of the areas coated with such coating materials.

In conjunction with the implementation of self-cleaning surfaces, coating materials on the basis of mineral paints, which are subject to constant decomposition on the surface, have been known for a long time. Due to this process, also known as "chalking," the surfaces regenerate constantly and dirt adhering to them is removed in the process of the decomposing coating. But these surfaces have the disadvantage that the irregular und, in some cases, complete decomposition of exposed areas results in patchy surfaces and that the chalking not only causes the rapid decomposition of the coating and, accordingly, shortened restoration intervals, but that also, upon contact with the coated surface, the materials touching it (e. g. clothing) are soiled with the decomposition products of the coating.

In addition to the self-cleaning coating materials based on mineral paints, self-cleaning coating materials having the form of silicone resin paints have also become known. Silicone resin paints form a hydrophobic surface which is barely moistened by precipitation water. Dirt particles are washed off the surface by the water draining off. But with such coating materials, it has proven to be a problem that the hydrophobicity required for the achievement of the self-cleaning properties is not fully developed until after weathering has taken place for several months, for that is the time it takes for the rain to completely wash out the water-soluble components contained in the coating material.

But that leads to the possibility of increased soiling taking place within the first few months of the completion of the coating. Such a tendency for soiling is particularly observed following long periods of dry spells, after which large quantities of dirt particles and pollutants are in the atmosphere and are absorbed by the precipitation water. The dirt particles are deposited on the surfaces capable of being moistened and result in an impairment of the appearance of the facades and other soiled surfaces onto which they are deposited.

In WO 00/39049, the creation of self-cleaning surfaces using coating materials of the kind described above is described. The coating materials described in this publication contain fillers exhibiting an at least bimodal particle size distribution, using, on the one hand, particles having a particle size of at least 5 μm and, on the other hand, particles having a particle size of max. 3 μm . The use of such coating materials has the effect that soiled rain water runs off the surface of an object and that dust particles deposited on the surface are pulled along by the water drops rolling off. In addition, the use of the coating materials described in the publication named above results in a permanently dry facade due to the running off of the rain water achieved by the use of the special fillers. This enables the prevention of damage due to moisture, especially on the weather sides of the facades. Furthermore, the achieved drying of the facades deprives microorganisms of an important element of their basic living conditions, namely water, allowing facade surfaces obtained by using the known coating materials to be protected from infestation with fungi, algae, lichens etc. in a natural manner, i. e. without the addition of biocides. A coating material comparable to the coating materials known from WO 00/39049 is also described in EP 0 772 514 B1. With the coating material described in this publication, a self-cleaning surface is obtained by producing a surface structure having elevations spaced apart 5 to 200 μm , using hydrophobic polymers or permanently hydrophobized materials, while making sure that the elevations are not capable of being detached by water or water containing detergents. This microstructure of the surface produces a self-cleaning property which is due to a so-called super hydrophobicity, caused by special microstructures. This property has become known as the "Lotus effect."

According to the publication named above, the desired surface structure can be obtained by an after-treatment of the surface, such as e.g. stamping, etching, milling or covering of the surfaces with dust, with it being required to ensure, in every case, that the thus obtained elevations cannot be removed by water or water containing detergents. The self-cleaning surface structure described in the publications mentioned above may be obtained on smooth surfaces as well as by using special sprays.

In WO 00/06633, coating materials for plastics based on inorganic binding agents and fillers are described. The coating materials set forth in the known publication may additionally contain photocatalytically active agents for self-cleaning by means of decomposition of organic soilings and superhydrophilics, while the binding agents used in the manufacture of the known materials are stable to the photocatalytic effect of the photocatalytically active agents.

In EP 0 916 411 A1, a coated product with a first coating layer and a second coating layer containing a photocatalytically active agent is described. The combination of two layers described in the above-mentioned publication produces a photocatalytically self-cleaning surface which is not even degraded by the photocatalytic action.

When using the coating materials known from EP 0 772 514 B1 and WO 00/39049, such as e.g. the sprays described for smooth surfaces, it turned out, however, that the originally observed outstanding self-cleaning properties can not be maintained permanently, even when, as emphasized in EP 0 772 514 B1, it is carefully made sure that the microstructure cannot be detached by water or water containing detergents.

In view of these problems in the state of the art, the invention is based on the problem of providing coating materials of the kind described above, whose self-cleaning properties are permanently maintained when they are exposed, from time to time, to rain, moving water or mechanical loads, such as wind.

According to the invention, this problem is solved by a further development of the known coating materials, which is essentially characterized in that the binding agent is at least partially catalytically degradable and the coating material contains at least one catalytically active agent.

In order to prevent the undesired chalking which occurs with the known coating materials based on mineral paints, the composition of the coating material is advantageously chosen such that the photocatalytic decomposition of the binding agent is equivalent to or below chalking level 1 in accordance with DIN EN ISO 4628-6. The permanent achievement of the desired self-cleaning properties may be ensured within the framework of the invention by producing a reduction of the thickness of the layer of the coating material by 0.1 μm or more, preferably 1 μm or more, per year by the photocatalytic decomposition of the binding agent when the coating material according to the invention is used as external coating, given exposed weathering pursuant to EN ISO 2810 (Klima Da, Probenkörper vertikal und dem Äquator zugewandt ausgerichtet [Sample vertical and oriented in the direction of the equator]).

The invention is based on the insight that the loss of the self-cleaning properties observed in the known coating materials is essentially due to the fact that, in addition to the impairments of the surface structure due to detachment of surface particles in the event of contact with water and/or detergents, which were mentioned in EP 0 773 514 B1, changes in the surface structure caused by mechanical loads may also be observed. These loads, caused, for example, by particles carried along with the air, can cause damage of the microstructure of facade surfaces which brings about the loss of the self-cleaning properties.

The use of the coating materials in accordance with the invention is accompanied by the automatic regeneration of surfaces damaged in such a way by the constant generation of new microstructures due to the catalytic decomposition of binding agent layers in between the filler particles. Based on the use of filler particles having a size and/or surface roughness in the range of less than 100 μm , these newly produced surface structures also exhibit the desired super hydrophobicity, allowing the formation of surfaces which maintain permanently self-cleaning properties. Here, the insight is utilized that the removal of surface layers, which precisely had to be avoided in accordance with EP 0 772 514 B1, may be taken advantage of in view of the preservation of the desired properties if the coating material exhibits particles having the desired surface structure or particle size.

The decomposition, by catalytic action, of binding agents occurring during the use of coating materials according to the invention does not result in the problems occurring with the mineral paints described above, because the speed of the catalytic decomposition of the binding agent may be controlled by the use of suitable catalytically acting agents so that an accumulation of decomposition products causing visible soiling does not occur due to the fact that these decomposition products are washed off in sufficient amounts and/or volatile materials are produced in the course of the catalytic decomposition, with said volatile materials not being deposited on the self-cleaning surface in the first place. The speed required to achieve the desired regeneration of the surfaces may be set in such a way, according to the selected particle size and/or surface roughness, that the catalytic decomposition of the binding agent does not result in shortened restoration intervals.

Overall, the use of the coating materials according to the invention achieves sufficient resistance to weathering despite the automatic regeneration of surfaces. Resistance to weathering of coating materials, such as paintwork, is understood to be their property of being able to withstand external influences of the weather that destroy the coating, such as light, UV radiation, temperature, oxygen, moisture and/or water. With conventional coating materials, resistance to weathering is achieved by subjecting coating components to which a photocatalytic action is attributed, such as titanium dioxide pigments, to a surface treatment in order to reduce the photocatalytic activity. In this way, highly stabilized pigments with excellent protective effect for coating materials are obtained with conventional coatings. Due to the remaining photocatalytic activity of these known materials, the layer thickness is reduced so slowly that it takes many years of external weathering for a reduction of the layer thickness by just a few μm to be observed.

The coating material according to the invention differs from these known materials in that the addition of a highly photocatalytically active agent produces a desired binding agent decomposition, with the speed of decomposition being set in such a way, by way of the selection of the binding agent and the photocatalytically active agent, that it is greater than the speed of decomposition of conventional materials with surface-treated photocatalytically active agents, but remains so low that the undesired chalking is avoided.

With respect to the desired adjustability of the speed of decomposition and/or the properties of the decomposition products, it has proven to be especially advantageous to have a binding agent that is at least in part photocatalytically degradable and to have a catalytically active agent that has at least one photocatalytically active metal oxide.

A photocatalytically degradable binding agent may exhibit an aqueous polymer dispersion, a polymer dispersion that is redispersible in water, a hydrophobic resin and/or a preliminary resin product.

The photocatalytically active agent may be present in the form of a photocatalytically active metal oxide. Taking into account the desired decomposition properties, the photocatalytically active agent may exhibit an oxide of titanium, zinc, iron, manganese, molybdenum and/or tungsten, preferably at a level of at least 60 weight percent, especially preferably at least 80 weight percent, specifically at least 90 weight percent in relation to the total quantity of the catalytically active agent. Further adjustability of the catalytical properties and the generated decomposition products can be achieved if the catalytically active agent exhibits at least one additive, specifically ion, selected from C, N, S and/or the group consisting of Pt, Rh, Mn, Cr, Ru, Ni, Pd, Fe, Co, Ir, Cu, Mo, Zr, Re, Ag and Au in the form of their oxides and/or halogenides, preferably at a level of 40 weight percent or less, especially preferably 20 weight percent or less, specifically 10 weight percent or less and more than 1 weight percent, preferably more than 2.5 weight percent, specifically 5 weight percent or more, in relation to the total weight of the catalytically active agent. This enables the stimulation of the catalytic property even with wave lengths e. g. in the visible range of the solar spectrum, ensuring the functioning of the coating even on the northern sides of a building, which face away from the sun. Photocatalyzers that are suitable for the decomposition of organic materials are described in DE 197 57 496 A1. The disclosed content of this publication with respect to the structure and composition of photocatalyzers is included here by explicit inclusion into this description.

In the use of photocatalytically degradable binding agents in conjunction with photocatalytically active metal oxides, it has proven to be especially advantageous that a self-renewing surface with lotus effect properties is obtained, with the self-cleaning being supported by an additionally occurring photocatalytic decomposition of organic soilings.

With respect to the achievement of particularly favorable self-cleaning properties, it has proven to be advantageous if the catalytically active agent exhibits zinc sulphide, zinc oxide or titanium dioxide, preferably in partially crystalline form or in the form of anatase.

Using coating materials in accordance with the invention, especially favorable self-cleaning properties are achieved if the filler contains particles having a size and/or surface roughness of 10 μm or less, specifically 1 μm or less, and especially preferably contains nano fillers in the form of highly disperse silica because outstanding hydrophobicity is obtained in this way. The coating material advantageously contains less than 60 weight percent, preferably less than 40 weight percent, and especially preferably less than 30 weight percent fillers with the desired particles sizes or surface roughnesses.

With respect to the achievement of the desired self-cleaning properties, it has furthermore proven to be advantageous if the coating material is formulated using an excess of binding agent. Accordingly, layers according to the invention consist of subcritical or critical formulations, which are characterized in that the contained filler consists at least partially of a nano particle, such as e. g. highly disperse silica. Those skilled in the art understand a critical or subcritical formulation to be a formulation in which possibly existing pigments, fillers and possible gaps are completely surrounded, resp. filled by the binding agent. The surface of the coating material or the film surface obtained by using respective coating materials is formed in the dried and hardened state of a closed layer of binding agents and fillers/pigments. A thus formed surface of a coating does not yet exhibit self-cleaning properties. By adding photocatalytically active metal oxides, such as the highly porous photocatalyzers described in DE 197 57 496, for the utilization of visible light or, in the simplest form, also using zinc sulphide, zinc oxide or titanium dioxide, preferably in partially crystalline form or in the form of anatase, the binding agent film is decomposed, starting at the outer layer of the external surface, due to the decomposition of organic components, catalytically induced by the effect of daylight or UV light. This degradation of binding agents exposes the preferably used nano fillers, which form a micro surface structure with hydrophobic properties. Advantageously, combinations of polymer dispersions and nano particles, such as e.g. highly disperse silica gels, so-called nano composites, may also be used. In the case of nano composites, the nano particles have already accumulated on the surface of the polymer dispersion particles.

The photocatalytic decomposition not only of the binding agent, but also of any organic dirt particles that might be on the surface, produces a significantly more effective and permanent self-cleaning function as compared to the state of the art. In the process, the surface is constantly renewed due to the constantly occurring decomposition of binding agents, and the decrease of the self-cleaning properties due to the loss of the microstructure is reliably prevented.

The photocatalytically induced decomposition is, however, highly reduced compared to the chalking surfaces described above, so that the disadvantages applicable to the chalking surfaces can be avoided.

Contrary to the coating material proposed in WO 00/39049, the coating material according to the invention may exhibit a filler with a monomodal particle size distribution with a mean particle diameter of 10 μm or less, specifically 1 μm or less, and especially preferably 0.1 μm or less.

In accordance with an especially preferred embodiment of the invention, the coating material exhibits 10 to 30 weight percent, specifically ca. 20 weight percent of a photocatalytically degradable binding agent, 2 to 30 weight percent, specifically 5 to 15 weight percent, and especially preferably ca. 10 weight percent of a filler having a mean particle size of 1 μm or less, specifically 0.1 μm or less, such as nanoscaled silica, 2 to 15 weight percent, specifically 3 to 8 weight percent, especially preferably ca. 5 weight percent of a photocatalytically active pigment, such as TiO_2 endowed, if necessary, with C, N and/or S, as well as optionally 0.01 to 0.1 weight percent, specifically 0.05 weight percent of a pigment distributor, 0.1 to 1 weight percent, specifically ca. 0.3 weight percent of a thickener, 5 to 3 weight percent, specifically 10 to 20 weight percent of another filler, such as e.g. a fine quartz filler, 10 to 20 weight percent, specifically 15 weight percent of a pigment, 2 to 8 weight percent, specifically ca. 6 weight percent of a hydrophobization agent, up to 4 weight percent of a solvent, up to 0.8 weight percent of a preservative and/or up to 35 weight percent of water. A preferred exemplary formulation of coating materials according to the invention is presented below:

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	Weight Percent
Water	26.6
Pigment distributor	0.05
Thickener	0.3
Binding agent	20
Quartz filler, fine	15
Nanoscaled silica	10
Pigment TiO_2	15
Photocatalytic pigment	5
Hydrophobization	6
Solvent	2
Preservation	0.05
	100.00

In summary, it can be stated that the disadvantage of all applications of self-cleaning surfaces taking advantage of the lotus effect is overcome by the invention by a combination of the nanotechnology producing the lotus effect and the photocatalysis. The lotus effect of a surface having a micro/nano structure achieves that the contact area of water becomes extremely small and the energy interaction between water and the surface falls under 1 %. The durability of such a coating is improved in accordance with the invention by adding nanoscaled particles, such as e.g. nanogels based on silica, to the coating material used for the creation of this coating structure, with said particles renewing the effective surface structure over and over again in the process of the continued weathering of the surface. For this process, the invention specifically uses photocatalysis, taking advantage of the insight that innumerable virtual nanoscaled surface layers are already present in the layer of one paint having a thickness of only ca. 150 μm due to the addition of nanoscaled fillers, so that the next surface layer automatically takes effect following the weathering of an external surface layer. In this process, the binding agent surrounding the nanoscaled fillers according to the invention is decomposed, causing (new) nanostructures to come to the surface.